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New bands in the A-X system of CuI and its dissociation energy

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New bands involving higher vibrational quanta of the ground as well as the excited state of the $A-X$ system of CuI have been observed These new observations have been utilized in a linear Birge-Sponer (L B.S) extrapolation to make a fresh estimate of the dissociation energy of CuI. The dissociation energies of all diatomic copper halides have been estimated theoretically using Rittner as well as Hulburt-Hirschfelder potential functions. The dissociation energy of CuI obtained in this work (~ 2.0 eV) has been discussed in the light of the earlier results

1. Introduction

The electronic spectrum of diatomic copper iodide molecule has been extensively studied by a number of workers (Mulliken 1925, Ritschl 1927, Nair & Upadhya 1966, Rao & Rao 1966, Nair 1967 and Pandey *et al* 1968) However in several aspects the spectroscopic study of CuI is still far from complete Thus, no information regarding the B state is available for CuI whereas this is very well characterised in other copper halides Gaydon (1968) recommended a value close to ~ 2 eV for the D_e of CuI, whreas L B S. extrapolation method as well as several thermochemical studies support a much larger value i e. 3 eV Finally in the previous study of the $A-X$ system of this molecule by Pandey *et al* (1968) several bands had been observed on the longer wavelength side of this system, these authors could not explain their origin The present series of investigations were undertaken to clarify some of these points and the present note deals with the assignments of these additional bands We have found that these new bands form an extension of the well known $A-X$ system of CuI and involve high vibrational levels of the ground and the excited states An interesting feature obtained in this analysis is that the new observations if included in L B S extrapolation do lead to a drastic reduction of the estimated dissociation energy

The dissociation energy of all the four diatomic copper halides have also been calculated using the empirical functions suggested by Rittner (1951) and by Hulburt-Hirschfelder (1941) to represent the potential energy curve It is observed that these estimates are in reasonable agreement with the experimentally observed values in all cases where reliable experimental values are known From

these studies we conclude that D_e of CuI should certainly be much less than 3 eV and is very nearly ~2.0 eV

2 Experimental Procedure

The bands were excited in a microwave discharge through the flowing vapour of pure Cu_2I_2. A pyrex glass tube, 10-12 cm in length and 0.8 to 1 cm in internal diameter with one end closed and the other end joined to another glass tube having a larger internal diameter (1.5 cm) was used. A pressure of the order of 10^{-2} torr was maintained in the discharge tube. A microwave oscillator (2450 MHz) yielding about 70 watts power was used to excite the bands. The spectrum was photographed on a 1.5 m Bausch and Lomb concave grating spectrograph having a reciprocal dispersion of 11.7 Å/mm. ORWO rapid (400 ASA) panchromatic film was used to record the bands and exposure times of 5-10 minutes duration were found adequate. Measurements were made on a Russian EZA-2 comparator (least count 0.001 mm) using iron arc lines as reference lines. Our measured wavenumbers are expected to be accurate upto ± 0.5 cm^{-1} for the unoverlapped bands.

3 Results

It is known from earlier studies (Mulliken 1925, Ritschl 1927, Pandey *et al* 1968) that the $A - X$ system of CuI lies in the region 4748 to 5650Å with the (0, 0) band at 5073Å. The highest values of v'' and vs involved in the bands observed by these workers were 8 and 12 respectively and they could not detect other bands on the higher wavelength side which involve higher vibrational levels of the ground and the excited state probably due to the poor intensity of their source.

In our experiment the source was quite intense and we could record even these weak bands with appreciable intensity within 5-10 minutes time. We could observe bands upto 5880Å. The emitter of these new bands as well as their vibrational assignments have been confirmed by the measurement of the shift between the two isotopic molecule ^{63}CuI and ^{65}CuI. It has been found that these new bands can be fitted very well in the Deslandres scheme of the $A - X$ system of CuI. The wavenumbers of these new bands, their vibrational assignments, visually estimated intensity as well as calculated and observed vibrational isotopic shift are given in table 1. The new bands alongwith the previously known bands are shown in figure 1.

4 Rittner Potential Function

The potential function proposed by Rittner (1951) reproduces very well the molecular constants and the ionic binding energy of the alkali halide molecules.

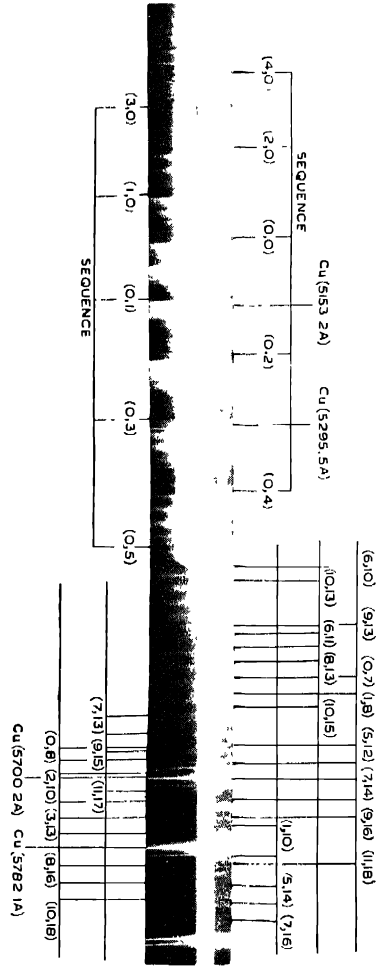

Fig 1 New bands in the A–X band system of CuI.

The nature of bonding in copper halide molecules is similar to alkali halides (probably with somewhat lower ionic contribution) Therefore, it was thought worthwhile to estimate the dissociation energy of copper halide molecules also using this potential function

Table 1. New bands in the A—X system of CuI and their assignments

Bands	I	Frequency corresponding to ^{63}CuI (cm^{-1})	Frequency corresponding to ^{65}CuI (cm^{-1})	Observed isotopic shift (cm^{-1})	Calculated isotopic shift (cm^{-1})
6, 4	0	18846.9			1.08
7, 7	0	19249.8			− 5.00
6, 7	0	19074.0	Atomic Line		− 6.83
6, 7	0	19074.0			− 6.83
6, 8	1	19821.4			− 9.52
6, 9	2	18569.0			−12.12
10, 13	0	18269.5			−15 36
6, 10	0	18320.9	18334.7	−13.8	−14.74
9, 13	0	18104.5	18122.2	−17.7	−18.10
6, 11	1	18076.0			−17 34
7, 12	1	18002.4	18021 6	−19 2	−18.10
8, 13	2	17935.2	17953.0	−17.8	−18 84
10, 15	0	17783.1	17803.2	−20.1	−20.50
0, 6	0	18145 3	18159.2	−13.9	−16.40
7, 13	1	17748.4	17779.2	−21.1	−2p.65
8, 14	1	17690 9	17724.5	−23.5	−21.40
9, 15	0	17620.0			−22.20
11, 17	0	17469.5	17492.3	− 22.8	−23.90
0, 7	0	17880.1	17908.2	−19.1	−19.04
1, 8	0	17842 8			−19 54
5, 12	4	17641.0	17662 7	−21.7	−21 82
6, 13	2	17580.2	17602.5	−22.3	−22.49
7, 14	1	17513 5	Atomic Line		−23.21
8, 15	1	17451.8	17473.8	−22.4	−23.90

Table 1. (*Contd.*)

Bands	I	Frequency corresponding to ^{63}CuI (cm^{-1})	Frequency corresponding to ^{65}CuI (cm^{-1})	Observed isotopic shift (cm^{-1})	Calculated isotopic shift (cm^{-1})
4, 12	1	17451 8	17173.4	−22 4	−23.80
9, 16	0	17382.0			−24.70
11, 18	0	17238 9	Atomic Line		−26 40
0, 8	0	17636 5	17657 7	−21 2	−21.79
1, 9	0	17590 9	17615 8	24 9	−22 20
2, 10	0	17549 5			22 67
5, 13	1	17394.2	17418.6	−24 4	−24 40
6, 14	1	17334 7	Atomic Line		−24 04
8, 16	0	17213 0			−25 45
9, 17	0	17148 3	17175 3	−27 0	−27 23
0, 9	0	17383 9			−24 31
1, 10	0	17343 5	Atomic Line		−24.76
3, 12	0	17253.3	Atomic Line		−25.80
5, 14	0	17148 3			−26 95
6, 15	0	17090.5	17117 5	27 0	−25 60
9, 16	0	17382 0			−24.71
6, 15	0	16852.1			−20 13
7, 17	0	17790.2	17821.1	− 30 9	− 30 81

The Rittner potential function can be expressed as

$$U(r) = -\frac{e^2}{r} - \left\{\frac{e^2(\alpha_1+\alpha_2)}{2r^4}\right\} - \left\{\frac{2e^2\alpha_1\alpha_2}{r^7}\right\} - \frac{c}{r^6} + A\exp\left(-\frac{r}{\rho}\right) \quad \ldots (1)$$

where α_1 and α_2 are the ionic polarizabilities of the two atoms and A and ρ are empirical constants for a given molecule. c is the attractive Vander Waal's constant and can be written as

$$c = \frac{3}{2}\alpha_1\alpha_2\left(\frac{I_2 E}{I_2 + E}\right) \quad \ldots (2)$$

where I_2 is the second ionization potential of copper and E is the electron affinity of the halogen atom

The primary condition for the applicability of this function is that the equilibrium internuclear distance $r_e > R$, the ionic radii of the negative ion. We have calculated the ionic radii of the negative ion by the method given by Rittner (1951) and the values thus obtained are given in table 2. It is observed that above condition for the applicability of this potential function is well satisfied in the case of copper halides.

We have also calculated the percentage ionic character using the expression given by Hannay-Smyth (see table 2) and the ratio of r_s/r_e (Herzberg 1950) (see Table 3) and both these suggest that the bonding in copper halides may be represented well by the Rittner function (1951).

Table 2 Molecular parameters used in the Rittner potential function

Molecules	Percentage ionic character	R (ionic radii of Halogens) Å	R (ionic radii of Halogens) $(\alpha)^{1/3}$ Å	Ionic radii* (Cu + Halogens) Å	Å	Å
CuF	49 03	1 04	1 02	2 00	1 743	0 17
CuCl	21 83	1 59	1.57	2 53	2.050	0 28
CuBr	17 20	1 74	1.69	2 70	2 173	0 26
CuI	10 86	2.02	1 93	2.81	2.334	0.28

* The sum of ionic radii is high since the ionic radius of Cu has been taken as the crystal ionic radius

Table 3. Dissociation energy of copper halides using Rittner potential function

Molecules	Values of r_s/r_e	D using Rittern potential function eV	D (Experimental) eV
CuF	2 02	4 23	4 47 ± 0*
CuCl	1.76	3.50	3 60 ± 0.25
CuBr	1 50	2.50	3 40 ± 0.25
CuI	1.36	1.87	2.00 ± 0 2

Hildenbrand, D L. 1968, *J. Chem. Phys.* **48**, 2457.

5. Method of Calculation

The method of calculation is similar to the procedure used by Varshni (1957, 1959) and by Varshni & Shukla (1961) for the alkali halides. The ionic binding energy of a molecule can be written as

$$D_i = \frac{e^2}{r_e}\left(1-\frac{\rho}{r_e}\right)+\frac{2e^2(\alpha_1+\alpha_2)}{r_e^4}\left(\frac{1}{4}+\frac{\rho}{r_e}\right)+\frac{14e^2\alpha_1\alpha_2}{r_e^7}\left(\frac{1}{7}-\frac{\rho}{r_e}\right)$$

$$+\frac{6c}{r_e^6}\left(\frac{1}{6}-\frac{\rho}{r_e}\right). \qquad \ldots (3)$$

The dissociation energy D_e of the molecule is related to the ionic binding energy by the relation

$$D_e = D_i - I + E \qquad \ldots (4)$$

We have calculated the dissociation energy of all the copper halide molecules by this method and they are compared with the experimental value in table 3. It is essential to point out at this stage that Rao *et al* (1968) using 3 parameter Lippincott potential function, and Nair & Singh (1971) using Szoke and Bartz's electronegativity potential function have also estimated this value and obtained 2.00 eV for the D_e of CuI.

6. Dissociation Energy of CuI

The dissociation energy of CuI calculated by the L.B.S. extrapolation using our recent data comes out to be 2.00 eV. In general this extrapolated value is expected to be higher than the actual value of the dissociation energy. Herzberg (1950) using the same extrapolation method as well as expressing D_e(CuI) in terms of D_e(AgI) has suggested a D_e(CuI) value $\sim$ 3 eV. His extrapolation was based on the old data of Mulliken (1925) and Ritschl (1927) and was limited upto $v'' = 12$. We could observe bands upto $v'' = 18$, and we find that in going from $v'' = 12$ to $v'' = 18$ the curve $G(v)$ versus v shows a tendency to approach the abscissa more rapidly than for $v'' < 12$. This additional data therefore lead to a much smaller value of D_e (CuI) than obtained from the older somewhat restricted data.

The D_e (AgI) had been earlier estimated as 2.01 eV by Terrien (1938) and by Butkow and Terinin (1928) using thermochemical method. This leads to a value 2.0 eV for D_e (CuI). Later on Metropolis and Beutler (1939) indicated that D_e(AgI) should be taken as 2.98 eV which would lead to the much higher value of 3.00 eV for D_e (CuI). Brewer and Lofgren (1950) performed similar experiments and concluded that D_e(AgI) should be reduced to (2.60$\pm$0.25 eV) and D_e(CuI) to 2.5$\pm$0.25 eV. But a direct determination of D_e (CuI) by the same method and by the same workers resulted in a very large value i.e. $<$3.27 eV. These authors have pointed out certain errors in the heat of vaporization of copper casting some

doubt on the reliability of this value. The atomic fluorescence experiment performed by Terinin (1930) gives a value ~ 2.20 eV. The present graphical extrapolation, atomic fluorescence as well as the method of fitting empirical functions to the RKRV curve all lead to $D_e(\mathrm{CuI}) \sim 2.0$ eV. The five parameter Hulburt-Hirschfelder potential function (1941) which has been shown to be the best representation of the potential energy curve of a diatomic molecule also leads to a similar value. We conclude therefore, that

$$D_e(\mathrm{CuI}) \sim 2.0 \pm 0.2 \text{ eV}.$$

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